CO_2 conversion to phenyl isocyanates by uranium(VI) bis(imido) complexes†‡

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ABSTRACT:

Uranium(VI) *trans*-bis(imido) complexes [U(κ⁴-{(^{tBu_2}ArO)$_2$Me$_2$-cyclam})(NPh)(NPh^R)] react with CO_2 to eliminate phenyl isocyanates and afford uranium(VI) *trans*-[O═U═NR]$^{2+}$ complexes, including [U(κ⁴-{(^{tBu_2}ArO)$_2$Me$_2$-cyclam})(NPh)(O)] that was crystallographically characterized. DFT studies indicate that the reaction proceeds by endergonic formation of a cycloaddition intermediate; the secondary reaction to form a dioxo uranyl complex is both thermodynamically and kinetically hindered.

Uranium complexes have emerged as attractive candidates for activation of the very stable C═O bonds of carbon dioxide,[1–3] which must occur during CO_2 functionalization. U(III) with appropriate supporting ligands can effectively reduce carbon dioxide, giving rise to various products that include an end-on-bound $CO_2^{\bullet-}$ U(IV) complex,[4] uranium oxo species,[5,6] carbon monoxide,[5,6] carbonates,[7,8] oxalates,[9] and isocyanate.[10] It was also demonstrated that U(IV) complexes with suitable ancillary ligands and functionalities can facilitate CO_2 insertion into U–E bonds (E = C, N, O, S).[11–14] Meyer and co-workers showed that U(V) terminal oxo complexes [{(^{R}ArO)$_3$tacn}U═O] are formed upon treatment of U(V) mono-imidos with CO_2, probably *via* [2+2] cycloaddition with elimination of isocyanates.[13,15] Similar CO_2 transformations have been observed with high oxidation state early transition metals, such as titanium imido complexes.[16–19] Activation of CO_2 by hexavalent uranium imido complexes has not yet been achieved, and in general CO_2 activation by U(VI) complexes is rare.[20] In such a rare case, the terminal nitride [U(Tren^{TIPS})(N)] reacted with CO_2 to yield a U(VI) oxo-cyanate complex by bond metathesis and cleavage of a C═O bond, with rapid decomposition of the product to [U^V(Tren^{TIPS})(O)].[20]

Several structurally characterized uranium(VI) imido complexes have recently been reported,[21–23] but reactivity studies of the U═NR bonds remain scarce,[24] particularly for U(VI) *trans*-bis(imido) complexes. Such *trans*-[RN═U═NR]$^{2+}$ systems notably are isoelectronic with thermodynamically stable uranyl, {O═U═O}$^{2+}$, but exhibit greater bond covalency.[25] It has been proposed that the inverse *trans*-influence (ITI)[26] of the two uranium–nitrogen multiple bonds stabilizes and reduces reactivity of the {RN═U═NR}$^{2+}$ moiety. Accordingly, Boncella and co-workers showed that treating [U(═N^{t}Bu)$_2$I$_2$(OPPh$_3$)$_2$] with PhN═C═O does not result in a uranium oxo complex but rather an imido transfer takes place to form [U(═N^{t}Bu)(═NPh)I$_2$(OPPh$_3$)$_2$].[27] We here demonstrate that U(VI) *trans*-bis(imido) complexes supported by a bis(phenolate) cyclam ligand react with CO_2 to produce stable *trans*-[O═U═NR]$^{2+}$ with elimination of aryl isocyanate.

Based on previous results for azobenzene activation with U(III) complex [U(κ⁶-{(^{tBu_2}ArO)$_2$Me$_2$-cyclam})I] (**1**), with formation of [U(κ⁴-{(^{tBu_2}ArO)$_2$Me$_2$-cyclam})(NPh)$_2$] (**2**),[28] the initial focus studies was on the synthesis of the new U(VI) bis(imido) [U(κ⁴-{(^{tBu_2}ArO)$_2$Me$_2$-cyclam})(NPh)(NTol)] (**3**), with a goal of assessing reactivity with CO_2. The reaction of 4-methylazobenzene (TolNNPh) with 2 equiv. of U(III) complex **1** in toluene at room temperature resulted in four-electron cleavage of the N═N double bond, affording the soluble bis(imido) [U(κ⁴-{(^{tBu_2}ArO)$_2$Me$_2$-cyclam})(NPh)(NTol)] (**3**) and the insoluble U(IV) compound [U(κ⁶-{(^{tBu_2}ArO)$_2$Me$_2$-cyclam})I][I], in a 1 : 1 ratio (Scheme 1).

Quality single crystals for X-ray diffraction were obtained by slow evaporation of a *n*-hexane/thf solution for two weeks. Refinement of the XRD data confirmed the expected U(VI) complex, with the phenyl imido and *p*-methyl phenyl imido ligands in a *trans* arrangement (N5–U1–N6 = 173.7(4)°) with an

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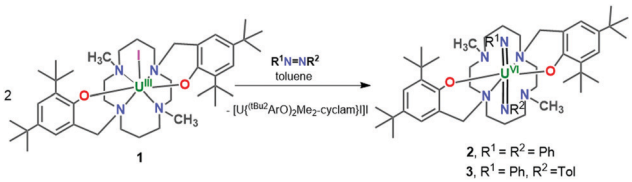
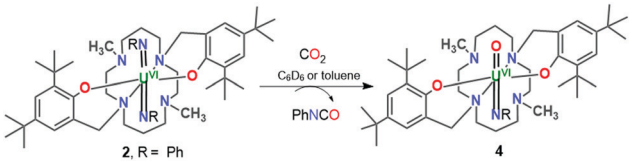
† A data set collection of computational results is available in the ioChem-BD repository[38] and can be accessed *via* https://doi.org/10.19061/iochem-bd-6-21.

‡ Electronic supplementary information (ESI) available: Computational and experimental details, NMR spectra, and detailed X-ray data. CCDC 1954718 and 1954719. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9cc07411b



Scheme 1 Synthesis of uranium(VI) bis(imido) complexes **2** and **3**.



Scheme 2 Synthesis of uranium(VI) oxo-imido complex **4**.

overall distorted octahedral geometry (Fig. S2 in ESI‡). Structural parameters of **3**, including short U–N_{imido} distances of 1.909(6) and 1.911(7) Å, are similar to those in the symmetric bis(imido) complex **2** (1.895(2) and 1.907(2) Å)[28] (structural parameters are in ESI‡ Table S2).

The ^{1}H NMR spectrum of **3** is characteristic of a diamagnetic compound, consistent with the asymmetric structure identified in the solid state. ^{1}H and ^{13}C NMR (see Fig. S3 and S4 in ESI‡) revealed two sets of resonances for the phenolate arms of $\{(^{tBu_2}ArO)_2Me_2\text{-cyclam}\}^{2-}$ and two distinct sets of resonances for the phenyl imido and *p*-methyl phenyl imido ligands.

Frozen brown solutions of **2** and **3** in benzene-d_6 were exposed to an excess of CO_2 (*ca.* 30 equiv.). Upon warming to room temperature, the colour of the solutions changed slowly from brown to dark cherry red. Following the reaction by ^{1}H NMR revealed that bis(imido) U(VI) complex **2** was completely consumed within 7 hours, with ingrowth of new *ortho*, *meta*, and *para* phenyl proton resonances at 5.19, 6.90 and 5.75 ppm, and aromatic resonances between 6.86 and 6.58 ppm, consistent with formation of a new uranium phenyl imido complex and elimination of phenyl isocyanate (Fig. S6 and S7 in ESI‡).

The ^{1}H NMR spectrum of the new complex exhibited integrated intensities for the $\{(^{tBu_2}ArO)_2Me_2\text{-cyclam}\}^{2-}$ and phenyl imido protons of 1 : 1, and revealed loss of the C_2 symmetry of the bis(phenolate) cyclam ligand. The benzylic protons gave rise to two AB systems with J_{AB} coupling of 12.1 and 12.3 Hz, and the four ^{t}Bu phenolate substituents appeared as 4 singlets, indicating that the two phenolate arms of $\{(^{tBu_2}ArO)_2Me_2\text{-cyclam}\}^{2-}$ have different chemical environments. In addition, two resonances for the NCH_3 protons were observed at 2.01 and 1.99 ppm and the phenyl imido protons showed only one set of resonances, which indicates free rotation about the N–C_{ipso} bond. The ^{13}C NMR data (Fig. S8–S10 in ESI‡) corroborated the ^{1}H NMR results, consistent with formation of U(VI) oxo imido complex [U(κ^4-$\{(^{tBu_2}ArO)_2Me_2$-cyclam$\}$)(NPh)(O)] (**4**).

An NMR tube-scale reaction of [U(κ^4-$\{(^{tBu_2}ArO)_2Me_2$-cyclam$\}$)(NPh)(NTol)] (**3**) with CO_2 showed that the bis(imido) complex is quantitatively converted to a mixture of mono-oxo imido [U(κ^4-$\{(^{tBu_2}ArO)_2Me_2$-cyclam$\}$)(NPh)(O)] (**4**) and [U(κ^4-$\{(^{tBu_2}ArO)_2Me_2$-cyclam$\}$)(NTol)(O)] (**5**), in approximately 1 : 1 ratio, along with the corresponding aryl isocyanates (Fig. S13 and S14 in ESI‡). Although most ^{1}H NMR resonances of the two uranium compounds overlap, it was possible to differentiate resonances that match the phenyl imido ligand of **4** from those of the methyl phenyl imido ligand of **5** (see Fig. S14 in ESI‡). Two of the ^{t}Bu phenolate resonances of **5** are at 2.08 and 1.86 ppm, with the other two centered at 1.57 ppm and overlapping with a ^{t}Bu resonance of **4**. ^{13}C NMR spectroscopy confirmed formation of the two U(VI) mono-oxo imido complexes, with the appearance of two pairs of carbon resonances for the C–O phenolates of $\{(^{tBu_2}ArO)_2Me_2\text{-cyclam}\}^{2-}$ (**4**: 166.75 and 166.56 ppm; **5**: 166.81 and 166.69 ppm).

The reaction of [U$\{(^{tBu_2}ArO)_2Me_2$-cyclam$\}$(NPh)$_2$] (**2**) with an excess of CO_2 in toluene resulted in a dark cherry red solid after evaporation of the solvent (Scheme 2). ^{1}H NMR of the crude solid was consistent with formation of **4** and a minor side product, perhaps from dimerization of phenyl isocyanate.[29] Recrystallization of the crude solid from hexane provided single crystals; X-ray diffraction confirmed the molecular structure as oxo imido complex [U(κ^4-$\{(^{tBu_2}ArO)_2Me_2$-cyclam$\}$)(O)(NPh)] (**4**) (Fig. 1).

Like complexes **2** and **3**, **4** exhibits an octahedral geometry about the uranium center, with the $\{(^{tBu_2}ArO)_2Me_2\text{-cyclam}\}^{2-}$ ligand adopting a κ^4-N_2O_2 coordination mode, and the oxo and phenyl imido are *trans*-oriented. The geometric parameters of the $\{RN{=}U{=}O\}^{2+}$ core (U1–O3 1.787(3) Å, U1–N5 1.879(3) Å, O3–U1–N5, 176.4(1)°) are comparable to those of previously reported [U(=NPh^{iPr_2})(O)Cl_2(tppo)$_2$] (U–O 1.778(2), U–N 1.847(3)),[30] while the U–O(aryloxide) and U–N(cyclam) bond distances are similar to those of **2** and **3**.

Crystallographically characterized *trans*-$[O{=}U{=}NR]^{2+}$ compounds are scarce, mostly prepared by oxygen atom transfer to U(IV) monoimido complexes or reductive cleavage of nitrite by a U(V) imido complex.[30–32] Treatment of U(VI) *trans*-bis(imido) [U(=N^{t}Bu)$_2I_2$(THF)$_2$] with water reagent B$(C_6F_5)_3{\cdot}H_2O$ also led to formation of a uranyl-like complex, [U(O)(=N^{t}Bu)I_2(THF)$_2$].[33]

We have shown here the first activation of CO_2 by a U(VI) imido complex, specifically a *trans*-bis(imido), with formation

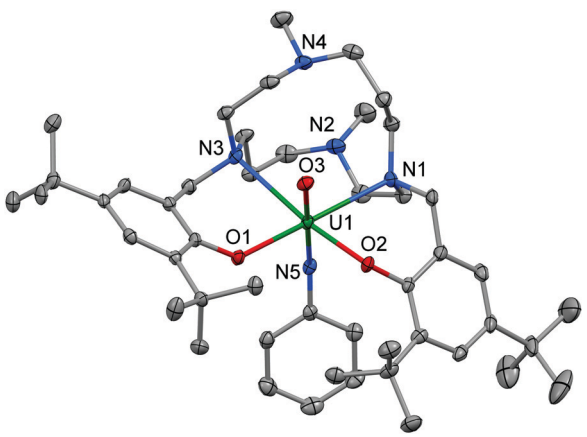


Fig. 1 Molecular structure of [U(κ^4-$\{(^{tBu_2}ArO)_2Me_2$-cyclam$\}$)(NPh)(O)] (**4**) with 50% probability thermal ellipsoids.

of a terminal uranium oxo bond. Selective formation of *trans*-$[O{=}U^{VI}{=}NR]^{2+}$ complexes **4** and **5** by multiple bond metathesis is presumably driven by a thermodynamic preference for U=O bond formation with release of aryl isocyanate. Complex $[U(\kappa^4\text{-}\{(^{t\mathrm{Bu}_2}\mathrm{ArO})_2\mathrm{Me}_2\text{-cyclam}\})(\mathrm{NPh})(\mathrm{O})]$ (**4**) did not exhibit reactivity upon CO_2 exposure in benzene-d_6, possibly reflecting enhanced stability of complex **4** due to a greater inverse *trans* influence upon U=O bond formation.[26]

To elucidate mechanistic aspects of the observed reactivity, the ADF program[34] was used with the rev-PBE-D3 density functional[35–37] to compute the CO_2 cycloaddition/isocyanate extrusion reaction pathway (see ESI‡ for Computational details). The starting reference state A (energy ≡ 0) is the two reactants infinitely separated (Fig. 2). van der Waals interaction between the reactants yields association complex B, which is followed by transition state, TS_B at 103.3 kJ mol^{-1} above A. The CO_2 insertion into a uranium imido site yields intermediate C at 59.5 kJ mol^{-1} above A. Cycloaddition *via* TS_B is a donor–acceptor process, as revealed by the frontier orbital in Fig. 3. A second transition state (TS_C) corresponds to cleavage of isocyanate intermediate C and leads to formation of the uranium imido mono-oxo complex **4** and phenyl isocyanate (D). TS_C presents

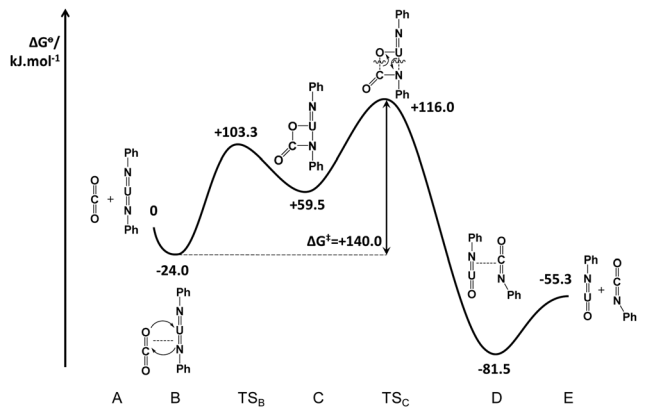


Fig. 2 Free energy profile for the reaction of $[U(\kappa^4\text{-}\{(^{t\mathrm{Bu}_2}\mathrm{ArO})_2\mathrm{Me}_2\text{-cyclam}\})(\mathrm{NPh})_2]$ (**2**) with CO_2.

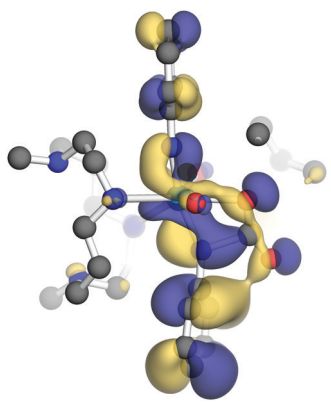


Fig. 3 A clipped detail of the HOMO−5 of TS_B showing the U(5f) → O and N → C donor–acceptor interactions with the incoming CO_2 molecule establishing new bonds.

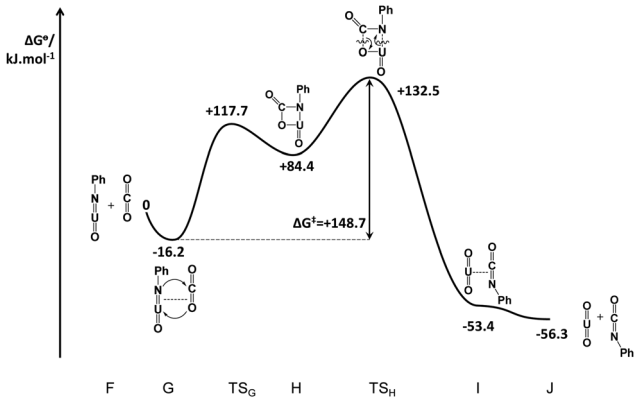


Fig. 4 Free energy profile for the reaction of $[U(\kappa^4\text{-}\{(^{t\mathrm{Bu}_2}\mathrm{ArO})_2\mathrm{Me}_2\text{-cyclam}\})(\mathrm{NPh})(\mathrm{O})]$ (**4**) with CO_2.

a substantial barrier of 116 kJ mol^{-1} above A and 140 kJ mol^{-1} above B, consistent with the observed slow kinetics at 25 °C. The free energy of 26.2 kJ mol^{-1} to dissociate complex **4** (steps D–E) is mostly due to the electronic contribution (ΔE = +31.2 kJ mol^{-1}). The interaction in D is presumably dominated by dispersion bonding between the uranium complex and phenyl isocyanate.

Formation of the oxo-imido complex **4** in D is a thermodynamic minimum, which evidently hampers subsequent addition of a second CO_2. The reaction profile for addition of CO_2 to **4** is shown in Fig. 4. Two aspects clearly differ from the profile in Fig. 2: formation of metallacycle intermediate H is more endergonic than for C ($\Delta\Delta G^\circ$ = +24.9 kJ mol^{-1}); and both transition states TS_G and TS_H are higher energy compared with TS_B and TS_C. In particular, rate determining transition state TS_H is 8.7 kJ mol^{-1} higher energy than TS_C. Notably, the exergonicity of step I (−53.4 kJ mol^{-1}) is not as favourable as for step D in Fig. 2 (−81.5 kJ mol^{-1}). Overall, it is apparent that CO_2 addition to complex **4** is both thermodynamically and kinetically hindered *vis-à-vis* CO_2 addition to bis(imido) complex **2**, consistent with observation of only the first process.

^{1}H NMR spectra were collected during reaction of **2** with CO_2 under pseudo-first-order conditions of a large CO_2 excess at constant concentration. A plot of the ln(molar fraction) of reagent as a function of time yields a pseudo-first-order rate. The rate was obtained for different temperatures such that using the Arrhenius equation and plotting $\ln k_{obs}$ *versus* $1/T$ provided a reaction activation energy E_a = 102 ± 12 kJ mol^{-1} (see ESI‡ for details). This E_a is somewhat smaller than the computed value of 140 kJ mol^{-1} in Fig. 2, which presumably reflects limitations of the computational and/or experimental methodologies (*e.g.* sample homogeneity during NMR acquisition). The effect of the higher pressure used in the experiments should be insignificant.

In conclusion, U(VI) *trans*-bis(imido) complexes supported by a bis(phenolate) cyclam ligand react with excess CO_2 to afford the *trans*-$[O{=}U{=}NAr]^{2+}$ species $[U(\kappa^4\text{-}\{(^{t\mathrm{Bu}_2}\mathrm{ArO})_2\mathrm{Me}_2\text{-cyclam}\})(\mathrm{NAr})(\mathrm{O})]$. DFT computational studies suggest that the reaction proceeds *via* endergonic formation of a [2+2] cycloaddition intermediate, with subsequent extrusion of phenyl isocyanate and formation of the U(VI) oxo-imido computed to be exergonic.

These reactions are unprecedented examples of activation and cleavage of CO_2 mediated by uranium(VI) imido complexes.

We acknowledge the financial support from the Fundação para a Ciência e a Tecnologia through projects UID/MULTI/00612/2019, UID/MULTI/04046/2019 and UID/MULTI/04349/2019, through the *post doc* fellowships SFRH/BPD/101840/2014 and SFRH/BPD/110419/2015 to LM and NAGB, respectively, and through RNEM – Portuguese Mass Spectrometry Network, ref. LISBOA-01-0145-FEDER-022125, also supported by the Lisboa Regional Operational Programme (Lisboa2020), under the PT2020 Partnership Agreement, through the European Regional Development Fund (ERDF). JKG was supported by U.S. Department of Energy, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences, Heavy Element Chemistry, at LBNL under Contract DE-AC02-05CH1123. The authors thank Dr M. C. Oliveira for the HR-MS analysis.

Conflicts of interest

There are no conflicts to declare.

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